

Thermodynamic Properties of Heisenberg Ferrimagnetic Spin Chains: Ferromagnetic-Antiferromagnetic Crossover

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We study thermodynamic properties of the one-dimensional Heisenberg ferrimagnet with antiferromagnetically exchange-coupled two kinds of spins 1 and $1/2$. The specific heat and the magnetic susceptibility are calculated employing a modified spin-wave theory as well as a quantum Monte Carlo method. The specific heat is in proportion to $T^{1/2}$ at low enough temperatures but shows a Schottky-like peak at mid temperatures. The susceptibility diverges as T^{-2} . We reveal that at low temperatures the model is regarded as a ferromagnet, while at mid temperatures it behaves like a gapped antiferromagnet.

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A great progress has been made in studying the qualitative difference [1] between the integer-spin and the half-odd-integer-spin Heisenberg antiferromagnets. Recently there has appeared brand-new attempts to explore the quantum behavior of mixed-spin chains with two kinds of spins. Low-energy properties of various mixed-spin chains with singlet ground states were analyzed [2] via the nonlinear- σ -model technique with particular emphasis on the competition between the massive and the massless phases. Mixed-spin chains with magnetic ground states serve us with another topic and have in fact attracted much current interests [3–8]. Since we expect a gapless excitation from the ferrimagnetic ground state, we there take little interest in the most naive problem whether the spectrum is gapped or gapless. Performing a numerical investigation by the use of conformal invariance, Alcaraz and Malvezzi [3] indeed predicted the appearance of quadratic dispersion relations for the mixed-spin Heisenberg ferrimagnets, which is consistent with a spin-wave calculation [4,5]. Actually the quadratic dispersion has explicitly been visualized employing a quantum Monte Carlo (QMC) technique [6] and an exact-diagonalization method [8]. Thus we may expect quantum ferrimagnets to behave like ferromagnets at low temperatures. However, several authors [4,5] have recently reported that quantum ferrimagnets have a non-trivial excitation branch gapped from the ground states as well as a gapless one, which stimulates us to investigate their thermodynamic properties. We show in this article that *the two distinct low-lying excitations result in a novel temperature dependence of the thermal quantities displaying both ferromagnetic and antiferromagnetic aspects*. The present study sounds more fascinating considering that all the mixed-spin-chain compounds synthesized so far exhibit ferrimagnetic ground states [9].

We consider alternatively aligned two kinds of spins S and s on a ring with antiferromagnetic exchange cou-

pling between nearest neighbors, which are described by the Hamiltonian

$$\mathcal{H} = J \sum_{j=1}^N (\mathbf{S}_j \cdot \mathbf{s}_j + \mathbf{s}_j \cdot \mathbf{S}_{j+1}) - g\mu_B H M, \quad (1)$$

where $M \equiv S^z + s^z \equiv \sum_{j=1}^N (S_j^z + s_j^z)$ is the total magnetization, N the number of the unit cells, μ_B the Bohr magneton, and we have set the g factors of the spins S and s equal to g . For the sake of argument, we assume throughout the manuscript that $S > s$. Applying the Lieb-Mattis theorem [10] to the Hamiltonian (1) with no external field, we find $(S - s)N$ -fold degenerate ground states. Therefore the model exhibits ferrimagnetism instead of antiferromagnetism. The gapless and the gapped excitations, respectively, lie in the subspaces of $M < (S - s)N$ and $M > (S - s)N$ and thus may be regarded as ferromagnetic and antiferromagnetic. In the case of $(S, s) = (1, 1/2)$, the gap to the antiferromagnetic branch was numerically estimated to be $1.759J$ [5,8].

Now we present QMC calculation of the thermal quantities at zero field. The recent field-theoretical argument [3] and density-matrix renormalization-group (DMRG) study [4] both suggest that the low-temperature properties of the model are qualitatively the same regardless of the values of S and s as long as they differ from each other. That is why we restrict our numerical investigation to the case of $(S, s) = (1, 1/2)$. We employ the QMC method based on the Suzuki-Trotter decomposition [11] of checkerboard type [12] and its numerical procedure has been detailed elsewhere [13]. We mainly calculate the $N = 32$ chain, which is long enough to discuss the bulk properties. Since the correlation length of the system is smaller than the length of the unit cell [4,5], the thermal quantities show no significant size dependence.

We show in Fig. 1 temperature dependences of the specific heat C (a) and the magnetic susceptibility χ (b).

Although the overall temperature dependences of the recent DMRG findings [4] are similar to ones of our QMC results, the two calculations are not in quantitative agreement with each other. We have confirmed that quantum transfer-matrix [14] calculation for short chains precisely reproduce the present QMC findings except for very low temperatures, where overshoot chains may pretend to be gapped. Furthermore high-temperature series-expansion calculation helps us to verify our numerical treatment. Within the up-to- t^{-3} approximation, the specific heat and the magnetic susceptibility are expanded as

$$\frac{C}{Nk_B} = t^{-2} + O(t^{-4}), \quad (2)$$

$$\frac{\chi J}{Ng^2\mu_B^2} = \frac{11}{12}t^{-1} - \frac{2}{3}t^{-2} + \frac{11}{36}t^{-3} + O(t^{-4}), \quad (3)$$

where $t \equiv k_B T/J$ with the Boltzmann constant k_B . The asymptotic curves (2) and (3) are also shown in Fig. 1, which convincingly fit the numerical results.

The usual spin-wave treatment diagonalizes the Hamiltonian (1) with no field as [4,5] $\mathcal{H} = E_g + \sum_k (\omega_k^- \alpha_k^\dagger \alpha_k + \omega_k^+ \beta_k^\dagger \beta_k)$, where $\omega_k^\mp = \omega_k \mp J(S-s)$ with $\omega_k = J[(S-s)^2 + 4Ss \sin^2(ak)]^{\frac{1}{2}}$, $E_g \equiv E_0 + E_1$ is the ground state energy with $E_0 = -2JSsNJ$ and $E_1 = \sum_k [\omega_k - J(S+s)]$, and a is the lattice spacing. α_k^\dagger and β_k^\dagger are the creation operators of the ferromagnetic and the antiferromagnetic spin waves with momentum k . The spin- S ferromagnetic Heisenberg chain exhibits the spin-wave excitations with a quadratic dispersion $\omega_k = 2JS[1 - \cos(ak)]$. Thus, only in the $S = 2s$ cases, the ferromagnetic branch of the spin- (S, s) ferrimagnets show exactly the same dispersion as the spin- s ferromagnets exhibit at small momenta in the unit of the unit-cell length being unity. Hence we expect the present model to behave like the spin-1/2 ferromagnet at low temperatures.

The precise low-temperature behavior of the spin-1/2 ferromagnet has been revealed by Takahashi and Yamada [15]. Numerically solving the thermodynamic Bethe-ansatz integral equations, they succeeded in expanding the thermal quantities by powers of $t^{1/2}$ as

$$\frac{C}{Nk_B} = 0.7815t^{\frac{1}{2}} - 2.00t + 3.5t^{\frac{3}{2}} + O(t^2), \quad (4)$$

$$\frac{\chi J}{Ng^2\mu_B^2} = 0.04167t^{-2} + 0.145t^{-\frac{3}{2}} + 0.17t^{-1} + O(t^{-\frac{1}{2}}), \quad (5)$$

which are also plotted in Fig. 1. Although the QMC calculation can not reach low enough temperatures, yet our findings allow us to conclude that *the present model is identified with the spin-1/2 ferromagnet at low enough temperatures*. We note that the lowest-temperature QMC estimates, which successfully imply the $T^{1/2}$ asymptotic behavior of the specific heat and the T^{-2} divergence of the magnetic susceptibility, were obtained through the improved algorithm [13] by spending forty million MC steps on each data point.

At mid temperatures in the specific heat, the antiferromagnetic aspect most clearly appears. The specific heat exhibits a sharp peak, rather than a broad one characteristic of ferromagnets, at $k_B T/J \simeq 0.74$ and therefore reminds us of the Schottky anomaly peculiar to the antiferromagnetic specific heat [13,14,16,17]. It is interesting to fit the QMC result to the Schottky-type specific heat

$$\frac{C}{Nk_B} = A \left(\frac{\Delta}{2k_B T} \right)^2 \text{sech}^2 \left(\frac{\Delta}{2k_B T} \right), \quad (6)$$

with Δ being set equal to the excitation gap to the antiferromagnetic branch of the present model, $1.759J$ [5,8], and a fitting parameter A . We find a fine fit with $A = 1.7$ as shown in Fig. 1 and thus recognize that *the mid-temperature behavior of the specific heat is well attributed to the gapped antiferromagnetic excitations*.

Now the ferromagnetic and the antiferromagnetic aspects of the model are both revealed. We inquire further into this picture developing the modified spin-wave (MSW) theory [18]. Introducing the additional constraint of the total magnetization being zero into the theory, Takahashi [19] not only overcame the difficulty in the conventional spin-wave theory but also succeeded in correctly evaluating the low-temperature behavior of various thermal quantities. His idea was further applied to the two-dimensional isotropic antiferromagnets [20,21] and thus opened the way for a quantitative argument of low-dimensional magnets in terms of the spin-wave picture. At finite temperatures, we replace $\alpha_k^\dagger \alpha_k$ and $\beta_k^\dagger \beta_k$ in the spin-wave Hamiltonian by $\tilde{n}_k^\pm \equiv \sum_{n^-, n^+} n^\pm P_k(n^-, n^+)$, where $P_k(n^-, n^+)$ is the probability of n^- ferromagnetic and n^+ antiferromagnetic spin waves appearing in the k -momentum state and satisfies $\sum_{n^-, n^+} P_k(n^-, n^+) = 1$ for all k 's. Then the free energy at zero field is expressed as

$$F = E_g + \sum_k (\tilde{n}_k^- \omega_k^- + \tilde{n}_k^+ \omega_k^+) + k_B T \sum_k \sum_{n^-, n^+} P_k(n^-, n^+) \ln P_k(n^-, n^+). \quad (7)$$

First, we consider minimization of the free energy (7) with respect to $P_k(n^-, n^+)$'s under the condition of zero magnetization,

$$\langle S^z + s^z \rangle = (S-s)N - \sum_k (\tilde{n}_k^- - \tilde{n}_k^+) = 0. \quad (8)$$

The free energy and the magnetic susceptibility at thermal equilibrium are obtained within a set of self-consistent equations:

$$F = E_g + \mu(S-s)N - k_B T \sum_k \sum_{\sigma=\pm} \ln(1 + \tilde{n}_k^\sigma), \quad (9)$$

$$\chi = \frac{(g\mu_B)^2}{3k_B T} \sum_k \sum_{\sigma=\pm} \tilde{n}_k^\sigma (1 + \tilde{n}_k^\sigma), \quad (10)$$

with $\tilde{n}_k^\pm = [e^{(\omega_k^\pm \pm \mu)/k_B T} - 1]^{-1}$, where μ is a Lagrange multiplier determined by the condition (8). The susceptibility has been obtained by calculating the thermal av-

erage of M^2 [18]. Equations (9) and (10) are expanded in powers of $t^{1/2}$ at low temperatures and result in

$$\frac{C}{Nk_B} = \frac{3}{4} \left(\frac{S-s}{Ss} \right)^{\frac{1}{2}} \frac{\zeta(\frac{3}{2})}{\sqrt{2\pi}} t^{\frac{1}{2}} - \frac{1}{Ss} t + \frac{15}{32(S-s)^{\frac{1}{2}}(Ss)^{\frac{3}{2}}} \left[\frac{(S^2 + Ss + s^2)\zeta(\frac{5}{2})}{\sqrt{2\pi}} - \frac{4\zeta(\frac{1}{2})}{\sqrt{2\pi}} \right] t^{\frac{3}{2}} + O(t^2), \quad (11)$$

$$\frac{\chi J}{N(g\mu_B)^2} = \frac{Ss(S-s)^2}{3} t^{-2} - (Ss)^{\frac{1}{2}}(S-s)^{\frac{3}{2}} \frac{\zeta(\frac{1}{2})}{\sqrt{2\pi}} t^{-\frac{3}{2}} + (S-s) \left[\frac{\zeta(\frac{1}{2})}{\sqrt{2\pi}} \right]^2 t^{-1} + O(t^{-\frac{1}{2}}), \quad (12)$$

where $\zeta(z)$ is Riemann's zeta function. In the case of $(S, s) = (1, 1/2)$, the expressions (11) and (12) coincide with Eqs. (4) and (5) up to the order t and the order t^{-1} , respectively, and therefore again show us *the identity between the present model and the spin-1/2 ferromagnet at low temperatures*.

The above-demonstrated MSW approach gives a satisfactory description at low temperatures, whereas we immediately find that it never applies away from the low-temperature region. For ferromagnets, the zero-magnetization constraint is not only convincing in that the thermal average of the magnetization should be zero at zero field, but also plays a role of keeping the number of bosons constant. This is not the case for ferrimagnets as well as for antiferromagnets [20,21]. Here the spin-wave treatment with the condition (8) still results in the divergence of the number of bosons at high temperatures. Can we control the number of bosons keeping the above-obtained low-temperature behavior unchanged and give a convincing description in a wider temperature region? We may answer yes replacing the condition (8) by

$$\langle : S^z - s^z : \rangle = (S+s)N - J(S+s) \sum_k \sum_{\sigma=\pm} \frac{\tilde{n}_k^\sigma}{\omega_k} = 0, \quad (13)$$

where the normal ordering is taken with respect to α and β . The spin-wave theory shows us that the classical staggered magnetization $(S+s)N$ is modified into $(S+s)N - 2\tau$ with a quantum spin reduction τ [5]. Equation (13) claims that the thermal fluctuation of the staggered magnetization be constrained to take the classical value. This is analogous to Eq.(8), which claims that the thermal fluctuation of the magnetization be the classical magnetization $(S-s)N$. We stress that the constraint (13) leads in fact to exactly the same expressions as Eqs. (11) and (12) at low temperatures. Now we again obtain a set of self-consistent equations:

$$F = E_g + \mu(S+s)N - k_B T \sum_k \sum_{\sigma=\pm} \ln(1 + \tilde{n}_k^\sigma), \quad (14)$$

$$\chi = \frac{(g\mu_B)^2}{3k_B T} \sum_k \sum_{\sigma=\pm} \tilde{n}_k^\sigma (1 + \tilde{n}_k^\sigma), \quad (15)$$

with $\tilde{n}_k^\pm = [e^{(\omega_k^\pm \pm \mu J(S+s))/\omega_k k_B T} - 1]^{-1}$, where μ is a Lagrange multiplier due to the condition (13).

We numerically solve Eqs. (13) and (14) in the thermodynamic limit, and visualize them for $(S, s) = (1, 1/2)$ in Fig. 2, where the QMC estimates are shown again. We find that the MSW calculation not only correctly describes the actual behaviors at low enough temperatures but also well reproduces the overall temperature dependences. The $T^{1/2}$ standing up, the Schottky-like peak, the T^{-2} decay of the specific heat, and the T^{-2} divergence, the T^{-1} decay of the susceptibility, they are all successfully described by our MSW approach. However, the spin-wave excitations underestimate the peak temperature of the specific heat. This is because the spin-wave theory results in the gap $\omega_{k=0}^+ = J$, which is smaller than the true value $1.759J$. In order to separately observe the contributions of the ferromagnetic and the antiferromagnetic modes, we regard $F_{AF} \equiv -k_B T \sum_k \ln(1 + \tilde{n}_k^+)$ and $\chi_{AF} \equiv (g\mu_B)^2 (3k_B T)^{-1} \sum_k \tilde{n}_k^+ (1 + \tilde{n}_k^+)$ as the antiferromagnetic contribution, while we define the ferromagnetic background as $F_F \equiv F - F_{AF}$ and $\chi_F \equiv \chi - \chi_{AF}$. Each contribution in the specific heat is numerically calculated from F_F and F_{AF} , respectively. We show in Fig. 2 the thus-obtained separate contributions. We clearly observe that $C_F \rightarrow C$ and $\chi_F \rightarrow \chi$ as $T \rightarrow 0$. On the other hand, due to the excitation gap, C_{AF} and χ_{AF} exponentially vanish as $T \rightarrow 0$. *It is due to the antiferromagnetic mode that the Schottky-like peak appears*. Finally, while the above consideration is enlightening, we admit that the present definition for C_F and C_{AF} may not be relevant at high temperatures, where the μ -term in Eq. (14) should not simply be incorporated into the ferromagnetic part. Such a ambiguity inevitably occurs because here the thermal quantities are obtained through the nonlinear equations.

We have investigated thermodynamic properties of the ferrimagnetic mixed-spin chains and revealed that the ferromagnetic and the antiferromagnetic aspects simultaneously lie in the model. It may also be emphasized that the spin-wave theory has so successfully been applied to the model of one dimension as to describe its whole thermal behavior. Not only direct observation of the thermal quantities but also neutron-scattering measurements of the antiferromagnetic excitations are fascinating experiments worth trying.

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FIG. 1. Quantum Monte Carlo Calculation (\circ) of the specific heat (a) and the magnetic susceptibility (b) as a function of temperature for the Heisenberg ferrimagnetic spin chain with alternating spins 1 and $1/2$ of $N = 32$. The solid lines: High-temperature series-expansion results for the present model within the up-to- $(J/k_B T)^3$ approximation. The dashed lines: Low-temperature Behavior [15] of the spin- $1/2$ ferromagnetic Heisenberg chain obtained by solving the thermodynamic Bethe-ansatz integral equations, where the thermal quantities are expanded by powers of $(k_B T/J)^{1/2}$. The specific heat and the magnetic susceptibility are plotted within the up-to- $(k_B T/J)^{3/2}$ and the up-to- $(J/k_B T)$ approximations, respectively. The dotted line: The Schottky-type specific heat with its gap being set equal to $1.759J$, that is, the energy difference between the ground state and the antiferromagnetic excitation branch of the present model.

FIG. 2. Modified spin-wave calculation (solid lines) of the specific heat (a) and the magnetic susceptibility (b) as a function of temperature for the Heisenberg ferrimagnetic spin chain with alternating spins 1 and $1/2$ in the thermodynamic limit, where both ferromagnetic and antiferromagnetic spin waves contribute to the thermal quantities. We effectively extract each contribution of the ferromagnetic and the antiferromagnetic spin waves and show them by dashed and dotted lines, respectively. Quantum Monte Carlo calculation (\circ) is again plotted for the sake of comparison.

Fig.1(a)

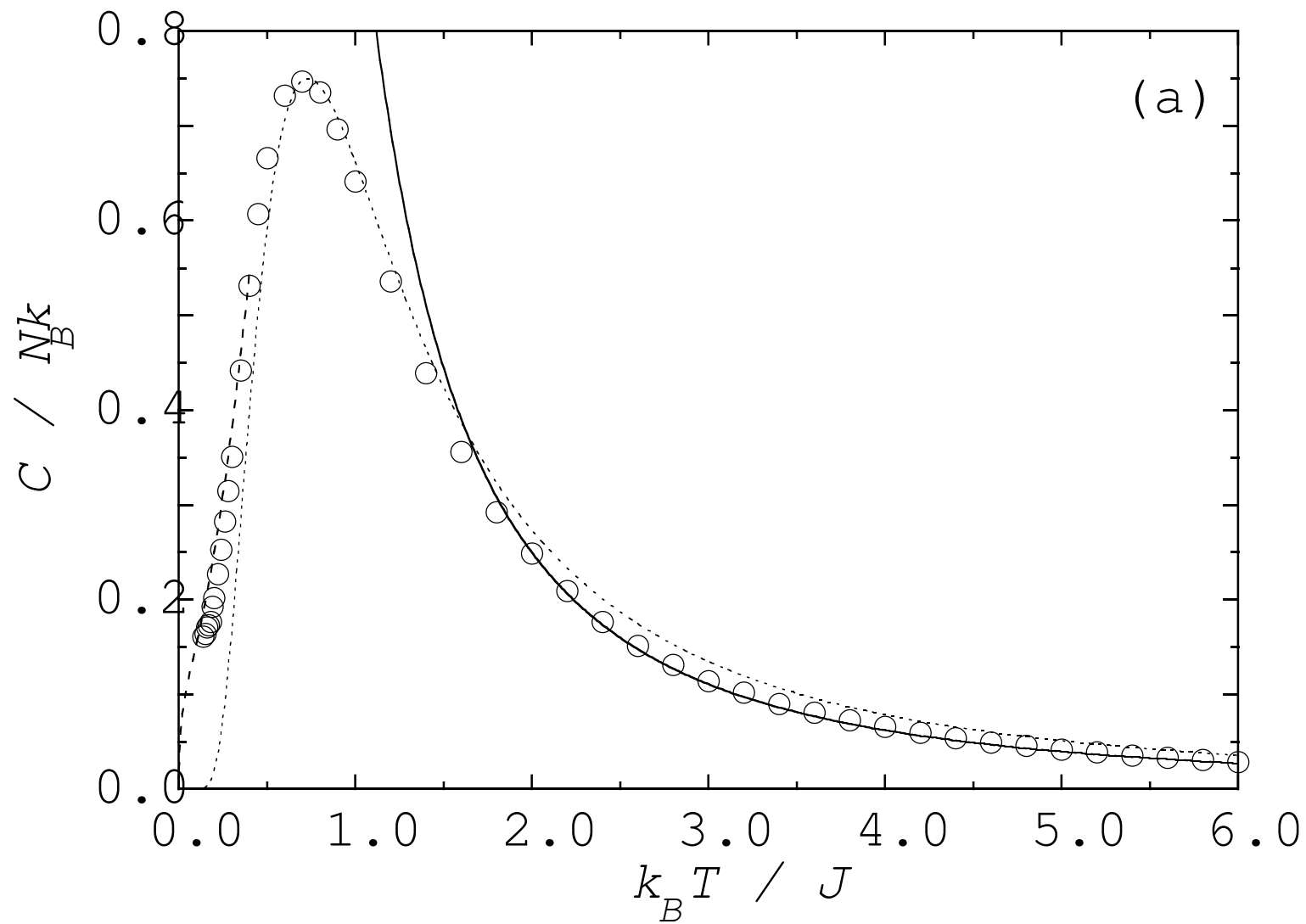


Fig.1 (b)

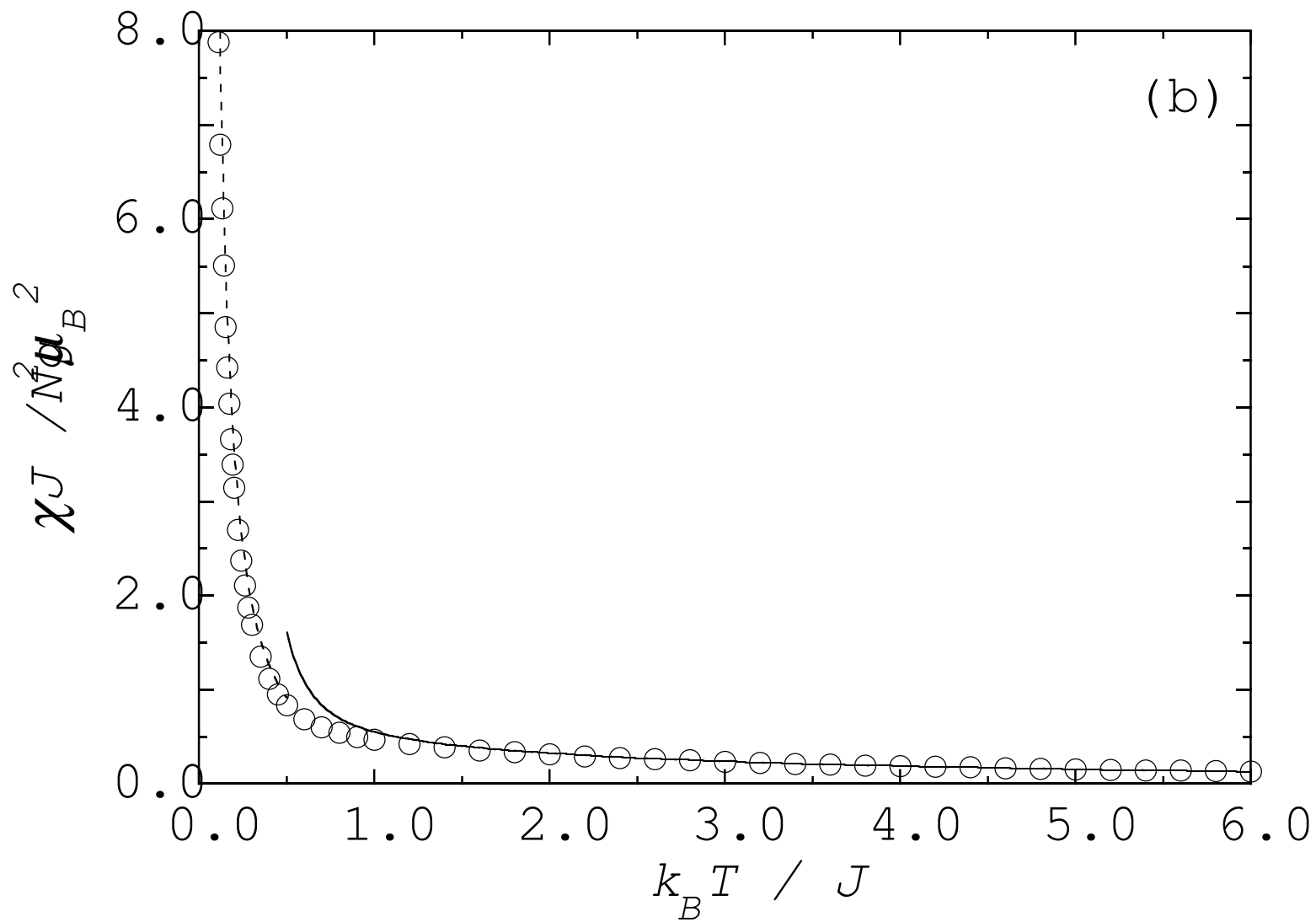


Fig.2(a)

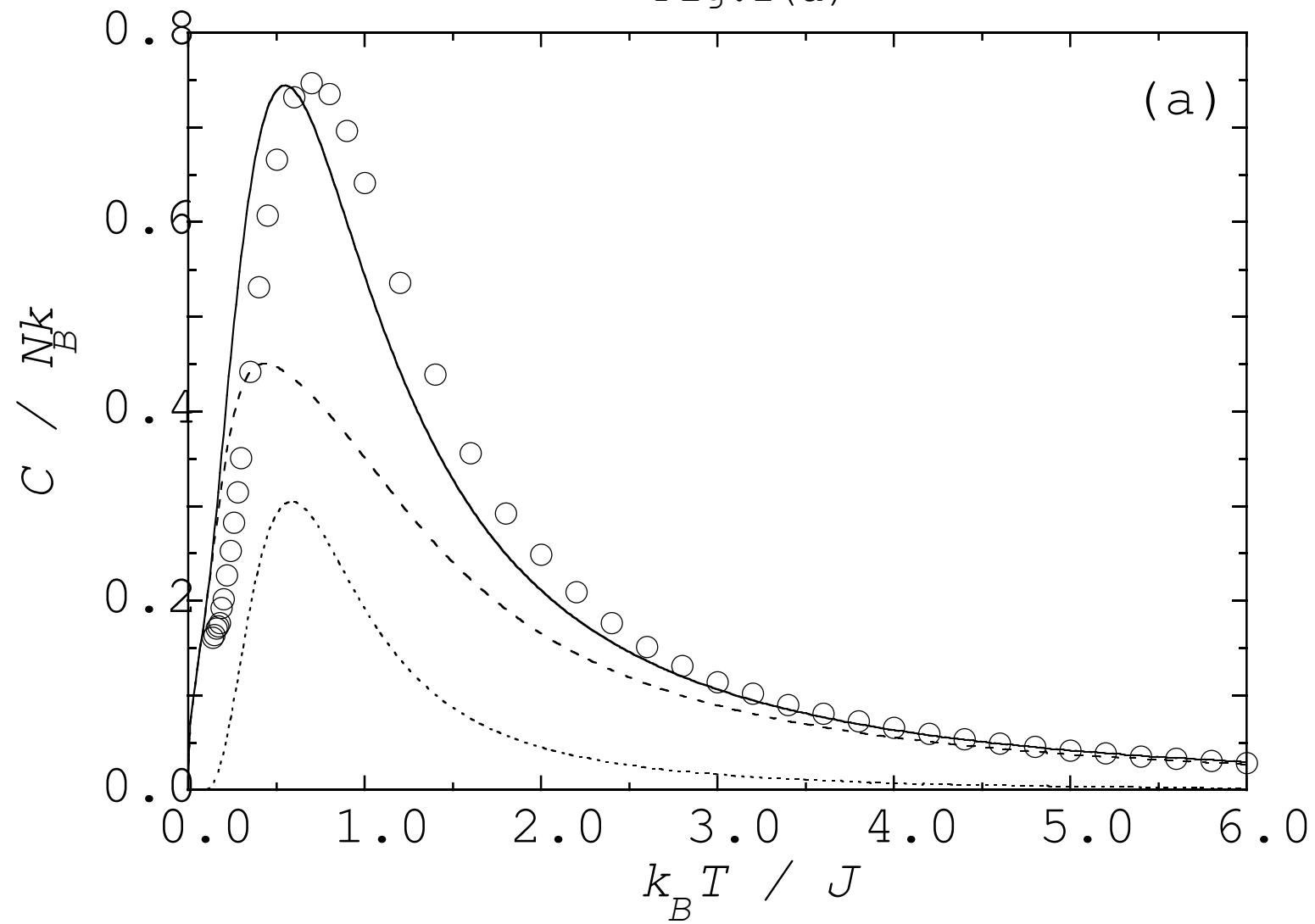


Fig.2 (b)

